HETEROCYCLES, Vol. 96, No. 4, 2018, pp. 641 - 663. © 2018 The Japan Institute of Heterocyclic Chemistry
Received, 29th October, 2017, Accepted, 5th March, 2018, Published online, 15th March, 2018
DOI: 10.3987/COM-17-13831

REACTIONS OF 1,3-THIAZINE-2,6-DITHIONES. PART 8.[1] FORMATION OF A NEW SERIES OF 2-PYRROLINE-4-THIONES BY THE REARRANGEMENT OF 1,3-THIAZINE-6-SPIRO-2'-THIIRANE-2-THIONES AND 2-METHYLTHIO-1,3(6*H*)-THIAZINE-6-SPIRO-2'-THIIRANES AND SOME RELATED REACTIONS

Tatsuo Yamamoto,* Hiroshi Miyamae, and Motomu Muraoka

Department of Chemistry, Faculty of Science, Josai University, 1-1 Keyaki-Dai, Sakado, Saitama 350-0295, Japan. E-mail: yukidai2@josai.ac.jp

Abstract – 1,3(6*H*)-Thiazine-6-spiro-2'-thiirane-2-thiones **2a-c** and 3',3'-disubstituted 2-methylthio-1,3-thiazine-6-spiro-2'-thiiranes **12a-f** were synthesized by the reaction of 1,3-thiazine-2,6-dithiones **1** or **11a-d**, which are 2-methylthio derivatives of thiazinedithiones **1**, with diazomethane derivatives. 1,3(6*H*)-Thiazine-6-spiro-2'-thiiranes **2a-c** and **12a-f** rearranged into a series of 2-pyrroline-4-thione derivatives **3a-c** and methyl 4-thioxopyrroline-1-dithiocarboxylates **13a-f** on treatment with a base or gentle heating. 2-Pyrroline-4-thione derivative **13c**, upon heating to 140 ºC for 1 h, reversely rearranged into the thiirane derivative **12c**. The structure of the 2-pyrroline-4-thione **13e** was determined by single-crystal X-ray analysis.

INTRODUCTION

Previously, we reported on the synthesis of 4,4-disubstituted thiazolizine-2,5-dithiones by the reaction of isothiocyanates with carbon disulfide in the presence of a strong base[2] and this reaction resulted in the first synthesis of several 2-pyrroline-4-thiones[3] by the transfragment reaction of the thiazolizine-2,5-dithiones with 3-aminoacrylonitrile or 3-aminocinnamonitriles bearing an alkyl substituent at position-4 of the benzene ring.

Prior to our report, there were only two reports concerning the synthesis of the thiazolizine-2,5-dithiones. One of those reports was presented by Shahak and co-workers,[4] and the other was the one by Shaumann and co-workers.[5] Renznikov and Volodarskii also reported a method of synthesis of 2-pyrroline-4-thione[6] in the same year (1990) as the report by us was presented.

Until now, there seems no other original report regarding the reactions of thiazolizine-2,5-dithiones including the formation of 1-aminoimidazolizine-2,5-dithiones and 2-pyrroline-4-thiones.

Further, the authors tried to synthesize various new types of heterocyclic and fused heterocyclic compounds by the reactions of 1,3-thiazine-2,6-dithiones[7-9] with many types of nucleophiles and found to be obtained fruitful results. Thus, in the reaction with 1,ω-diaminoalkanes, the 1,3-thiazine-2,6-dithiones produced imidazo[2,1-*b*]pyrimidine-5-thiones, pyrimido[2,1-*b*]-pyrimidine-4-thiones, pyrimido[2,1-*b*][1,3]diazepine-4-thiones, and pyrimidodiazepine-4-thiones.[10]

In contrast, the same 1,3-thiazine-2,6-dithiones yielded pyrimidobenzimidazole-4-thiones in the reaction with *o*-phenylenediamine.[10]

Various pyrimidine-2,4-dithione derivatives were formed by the reaction of these thiazinedithiones with hydrazines, hydroxylamine, and semicarbazide.[11] Thiosemicarbazide took a different reaction course with those thiazinedithiones and yielded triazolopyrimidines.[11]

In reaction with 3-aminoacrylonitriles, the thiazinedithiones gave two kinds of products depending on the solvent used. When the reactions were conducted in THF, pyrimidine-4-thiones were obtained as a result of transfragment reaction[12] and in the reaction using DMF as a polar aprotic solvent, 2-cyanomethyl-2,3-dihydro-1,3-thiazine-6-thiones were formed. Subsequent treatment of these 2,3-dihydro-1,3-thiazine-6-thiones with a strong base eliminated H_2S and 4-thiopyridone derivatives[13] were produced.

1,3,5-Thiadiazine-4-thiones were also formed by the same transfragment reaction between the thiazinedithiones and thioureas.[14] A unique reductive alkylation reaction of thiols with the thiazinethiones produced 2-alkylthio-2,3-dihydro-1,3-thiazine-6-thiones.[15]

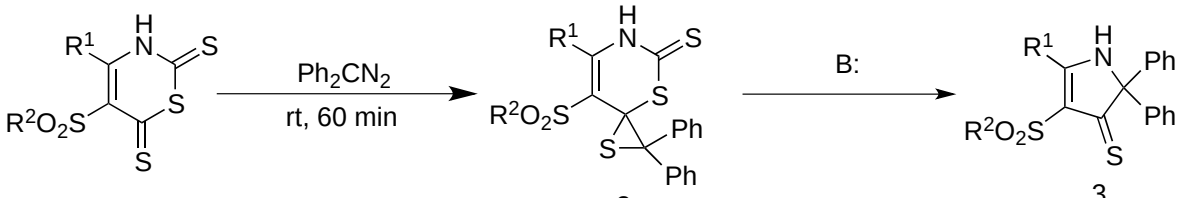
In addition to the formation of these heterocyclic and fused heterocyclic compounds summarized above, the thiazinedithiones, in reactions with primary amines, alcohols or thiols, ring opening reactions also took place and yielded 3-thioureidocinnnamthioamides and 3-[bis(alkylthio)methyleneamino]dithio-cinnamic acid esters respectively.[16]

RESULTS AND DISCUSSION

Our current interest is focused on the synthesis of new types of heterocyclic compounds through [3+2] cycloaddition of the 1,3-thiazine-2,6-dithiones **1** with 1,3-dipolar compounds such as phenyldiazoethane and diphenyldiazomethane.

Thus, when the 1,3-thiazine-2,6-dithiones **1a-c** bearing an aryl group at position-4 and an arylsulfonyl group at position-5, were allowed to react with diphenyldiazomethane at room temperature without catalyst, 3',3'-diphenyl-1,3(6*H*)-thiazine-6-spiro-2'-thiiranes **2a-c** were isolated in fair to good yields. These 6-spiro-2'-thiirane derivatives **2** were, probably, formed via two steps: first, [3+2] cycloaddition

between diphenyldiazomethane and the C=S double bond at position-6 of the thiazinedithiones produced unstable intermediate 1,3,4-thiadiazole derivatives, and second, the generated 1,3,4-thiadiazole derivatives promptly eliminated N_2 to yield the thiiranes **2** (**Scheme 1**).



Compd.	R^1	R^2
1a	Ph	Ph
1b	Ph	*p*-tolyl
1c	*p*-tolyl	*p*-tolyl

Compd.	Yield(%)
2a	70
2b	67
2c	80

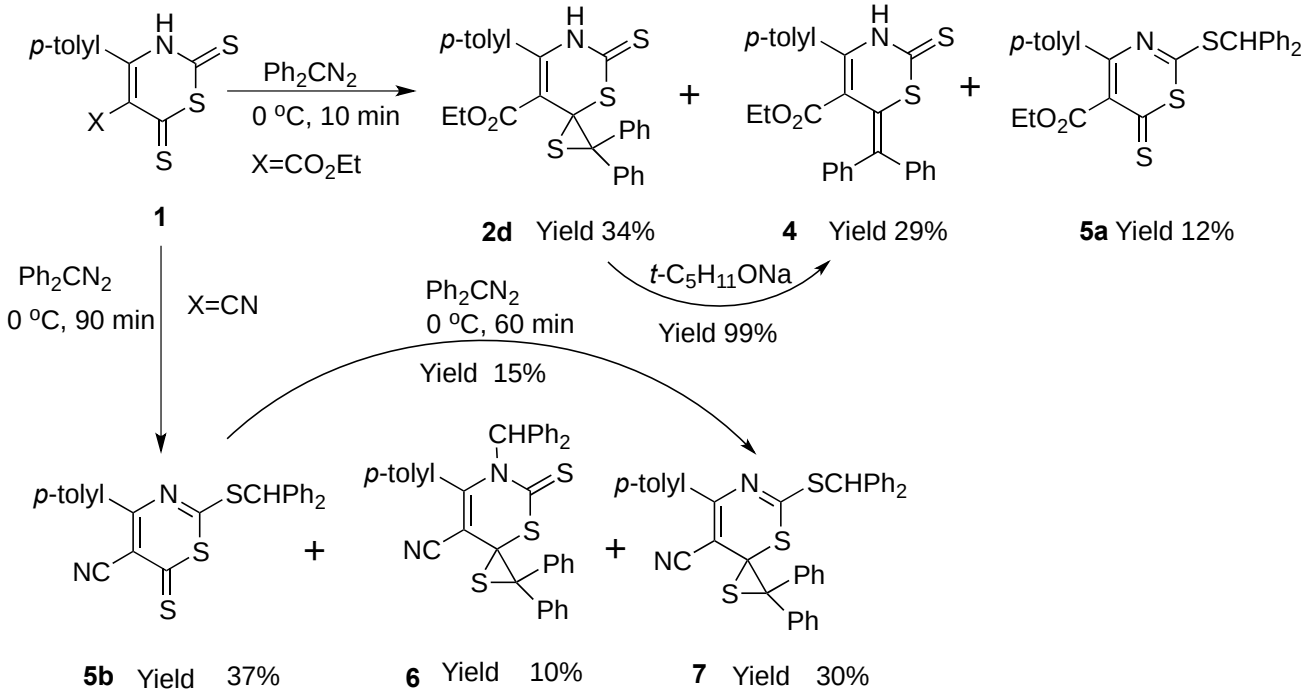
Compd.	Yield(%)
3a	61
3b	67
3c	67

Scheme 1

Furthermore, when these 6-spiro-2'-thiiane derivatives **2a-c** were treated with a strong base such as sodium 1,1-dimethylpropoxide, which is very strongly basic and soluble in almost organic solvents and yet has no nucleophilicity, in THF, a new class of pyrroline-4-thione derivatives **3a-c** were formed in fairly good yields through unique rearrangement of the 6-spiro-2'-thiiane derivatives **2a-c** and subsequent rapid dedithiocarboxylation of the generated intermediates (2-pyrroline-4-thione-1-dithiocarboxylic acids formed by the rearrangement of the thiiranes **2**. Refer to (**Scheme 8**).

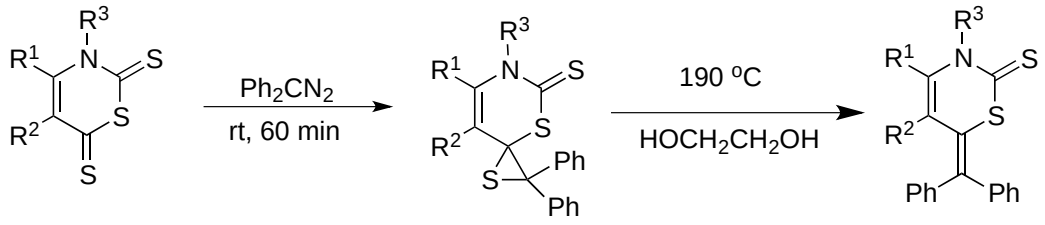
The 6-spiro-2'-thiirane derivative **2d** bearing an ethoxycarbonyl group at position-5 was also prepared by the reaction of 1,3-thiazine-2,6-dithione **1d** with diphenyldiazomethane together with two other compounds, ethyl 6-diphenylmethylene-2-thioxo-4-*p*-tolyl-1,3-thiazine-5-carboxylate **4** and ethyl 2-(diphenylmethylthio)-1,3-thiazine-5-carboxylate **5a.** The spiro-2'-thiirane derivative **2d**, however, never afforded the expected pyrroline-4-thione derivative under reaction conditions similar to that used in the formation of compounds **3a-c**, but it afforded an alkene-type product **4** as sole product by desulfurization in quantitative yield.

In the reaction with diphenyldiazomethane, thiazinedithione **1e** having a cyano group at position-5, also did not produce the corresponding pyrroline-4-thione derivative, but gave only 2-(diphenylmethyl)thio-1,3-thiazine-4-thione **5b** and two kinds of spirothiiranes **6** and **7** (**Scheme 2**).



Scheme 2

In addition, spirothiiranes **9a-d** which were synthesized by the reaction similar to the reaction of *N*-substituted thiazinedithiones **8** with diphenyldiazomethane, never rearranged to the corresponding pyrroline-4-thione derivatives on heating in both boiling toluene and boiling xylene; the starting spirothiiranes were recovered quantitatively. However, on heating to 190 °C in boiling ethyleneglycol, the spirothiiranes **9a-d**, yielded alkene-type compounds **10a-d** by thermal desulfurization (**Scheme 3**).



8 9 10

Compd.	R^1	R^2	R^3
8a	Me	CN	Me
8b	Ph	CN	Me
8c	*p*-tolyl	CN	Me
8d	Ph	CO_2Et	Ph

Compd.	Yield(%)
9a	98
9b	89
9c	93
9d	71

Compd.	Yield(%)
10a	72
10b	57
10c	97
10d	96

Scheme 3

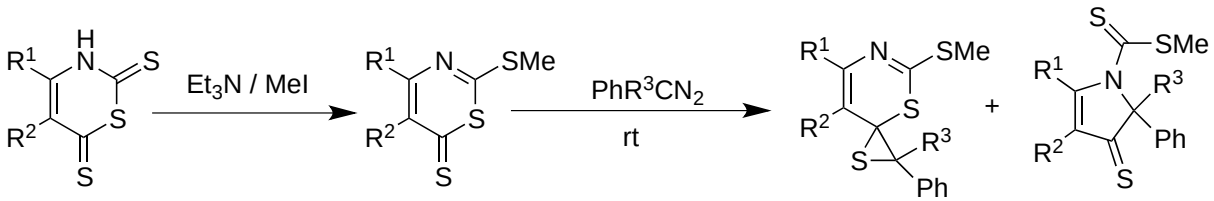
2-Methylthio-4-phenyl-5-phenylsulfonyl-1,3-thiazine-6-thione (**11b**), which was prepared by methylation of the corresponding 1,3-thiazine-2,6-dithione **1**, and upon standing a solution of the methylthio

derivative **11b** and diphenyldiazomethane in THF at room temperature, the pyrroline derivative **13b** was obtained directly in quantitative yield.

The methylthio derivatives **11a**,**c-e** are very important because these compounds **11a**,**c-e** are converted into the spiro-2'-thiiranes **12a**,**c-e** which are able to rearrange to the pyrroline-4-thione derivatives **13a**,**c-e**.

High yields of thiiranes **12a**,**c-e** were synthesized under the same reaction conditions as used for the formation of the pyrroline derivative **13b**. Thiiranes **12b** and **12f** were, however, never obtained under the same reaction conditions. Instead, methyl 4-thioxopyrroline-1-dithiocarboxylate derivatives **13b** and **13f** were formed as sole product in high yields.

The 2-methylthio derivatives **11b** whose thiazine moiety bears a strongly electron-withdrawing phenylsulfonyl substituent at position-5 is unusually reactive. Thiirane **12b** was obtained as the main product for the first time when a solution of 1,3-thiazine-6-thione derivative **11b** was allowed to react with diphenyldiazomethane in THF at –50 °C.



Compd.	R^1	R^2
11a	Ph	SO_2Me
11b	Ph	SO_2Ph
11c	Ph	CO_2Et
11d	*m*-tolyl	CN

Compd.	R^1	R^2	R^3	Yield	Compd.	Yield
12a	Ph	SO_2Me	Ph	94%		
12b	Ph	SO_2Ph	Ph	0%	**13b**	98%
12b				(71%)*		(20%)*
12c	Ph	CO_2Et	Ph	96%		
12d	*m*-tolyl	CN	Ph	70%		
12e	Ph	SO_2Me	Me	97%		
12f	Ph	SO_2Ph	Me	0%	**13f**	97%

* at -50 °C

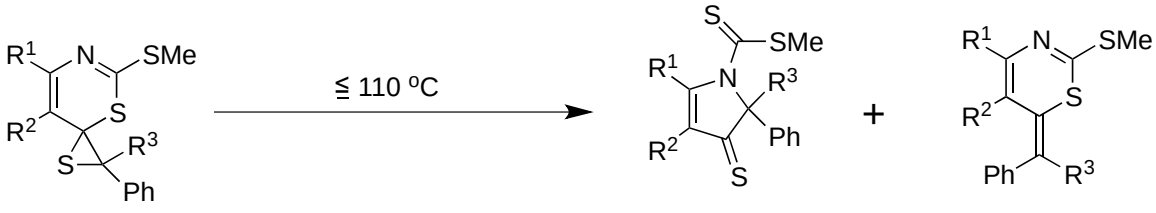
Scheme 4

This marked difference in the reaction results of (2-methylthio)thiazinethione **11b** towards each diazomethane derivative was assumed to be due to the intermediate thiirane derivative **12b** which has a phenylsulfonyl group at position-5 makes it much more reactive than other thiirane derivatives **12a**,**c-e** under respective reaction conditions. Therefore, as soon as thiirane derivative **12b** was formed, it would rearrange instantaneously into pyrroline-4-thione derivatives **13b** (**Scheme 4**).

To the contrary, all of other thiiranes **12a**,**c-e** are very stable at room temperature and were isolated in

high yields without converting it into the corresponding pyrroline-4-thione derivatives **13a**,**c-e**. However, these very stable thiiranes **12a**,**c-e** rearranged, in the end, to their respective pyrroline-4-thione derivatives **13a**,**c-e** upon refluxing in boiling toluene, accompanied by the desulfurized products, 6-(diphenylmethylene)-1,3-thiazine derivatives **14a**,**c**,**d** (**Scheme 5**).

Compared with the yields of the other pyrrolinethione derivatives **13**, the yield of compound **13d** was abnormally low because desulfurized by-product **14d** formed competitively in the fixed reaction conditions.



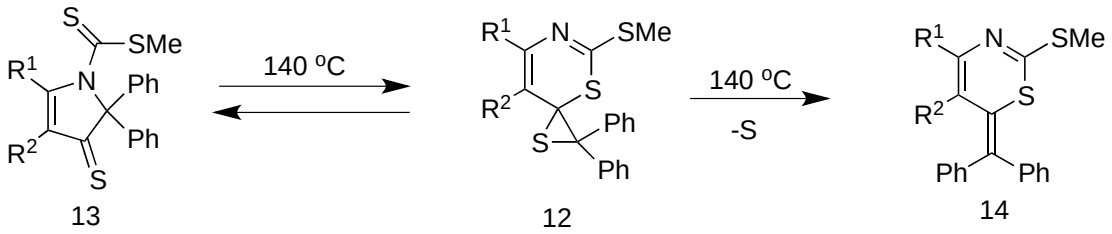
12 13 14

Compd.	R^1	R^2	R^3	temp.	time	Compd.	Yield	Compd.	Yield
12a	Ph	SO_2Me	Ph	110 °C	4 min	**13a**	76%	**14a**	19%
12b	Ph	SO_2Ph	Ph	rt	20 min	**13b**	100%		
12c	Ph	CO_2Et	Ph	110 °C	2 h	**13c**	69%	**14c**	25%
12d	*m*-tolyl	CN	Ph	110 °C	20 h	**13d**	41%	**14d**	40%
12e	Ph	SO_2Me	Me	80 °C	4 min	**13e**	100%		

Scheme 5

Furthermore, when pyrroline-4-thione derivative **13c** was refluxed in xylene at 140 °C, the 6-spiro-2'-thiirane derivative **12c** was obtained in 35% yield by reverse rearrangement of the pyrroline derivative **13c**. This reversible rearrangement that occurred between compound **12c** and **13c** is a very rare phenomenon and the authors tried persistently to find other cases of reversible rearrangement. However, the other pyrroline-4-thione **13d** was never converted into 1,3(6*H*)-thiazine-6-spiro-2'-thiirane-2-thione **12d**. Instead, pyrroline-4-thione **13d** yielded only desulfurized 1,3-thiazine derivatives **14d** in low yield. The pyrrolines **13a**,**b**,**f**, however, never changed on heating to 140 °C (**Scheme 6**).

In the case of the formation of 1,3-thiazine derivatives **14c**,**d** upon heating the pyrroline derivatives **13c**,**d** in boiling xylene, it is inevitable that spiro-2'-thiirane-2-thiones **12c**,**d**, the precursors for the compounds **14**, are formed by the inverse rearrangement of pyrroline derivatives **13c**,**d**. The fact that the compound **12d** was not isolated even in trace quantities is because of the following reason: under the fixed reaction conditions, as soon as the compound **12d** formed, this thiirane **12d** rapidly decomposed into 1,3-thiazine derivative **14d** by thermal desulfurization.



13 12 14

Compd.	R^1	R^2	time	Yield	Compd.	Yield	Compd.	Yield
13c	Ph	CO_2Et	1 h	42%	**12c**	35%	**14c**	0%
13c	Ph	CO_2Et	24 h	14%	**12c**	0%	**14c**	48%
13d	*m*-tolyl	CN	1 h	76%	**12d**	0%	**14d**	18%
13d	*m*-tolyl	CN	24 h	0%	**12d**	0%	**14d**	71%

Scheme 6

The structure of representative pyrroline-4-thione derivative **13e** was determined by X-ray crystal structure analysis in addition to confirmation by IR, ^{1}H- and ^{13}C-NMR spectra and elemental analysis. The ORTEP view of compound **13e** is shown in Figure 1. The detailed data for the single-crystal X-ray analysis of pyrroline derivative **13e** are shown in the Experimental Section (**Figure 1**).

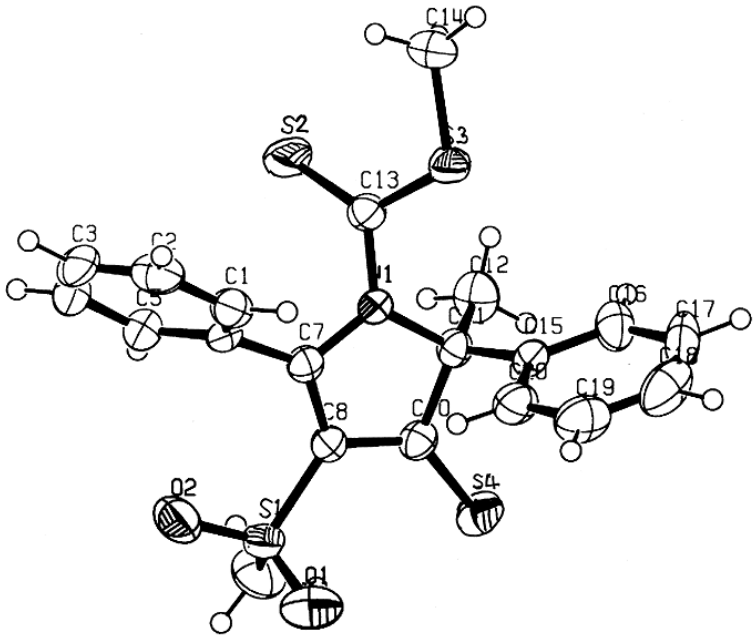
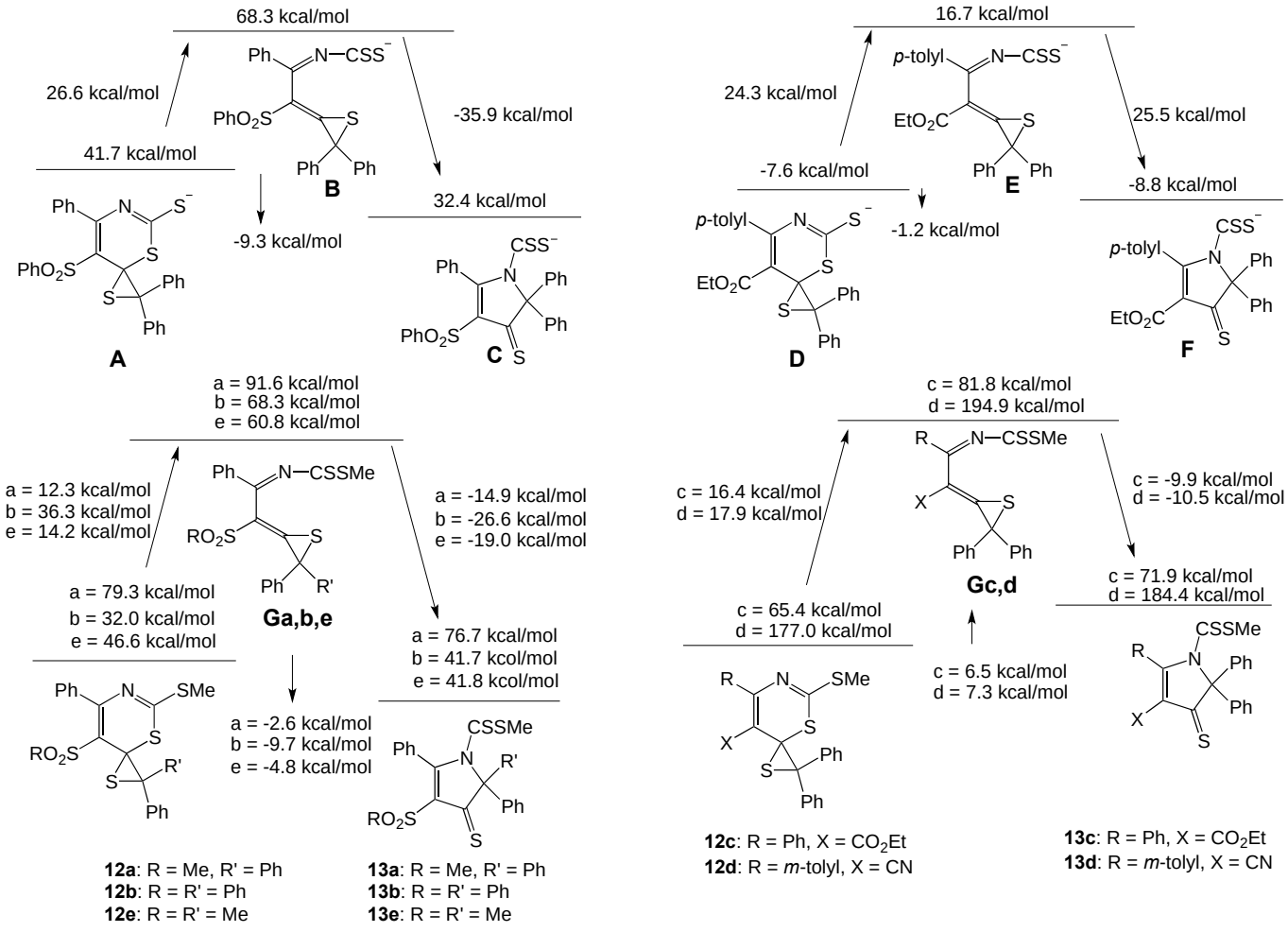


Figure 1. ORTEP view of compound **13e**

The marked difference that the above-mentioned rearrangement takes place or does not, depending upon the substituent at position-5 of *N*-unsubstituted 3',3'-diphenyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane derivatives **2** is, seemingly, curious. However, from the result of calculated heat of reaction based on the

heat of formation by MOPAC PM5, it is ascertained obviously that the rearrangement yielding a new series of 2-pirrolime-4-thiones takes place or does not (**Scheme 7**).



Scheme 7

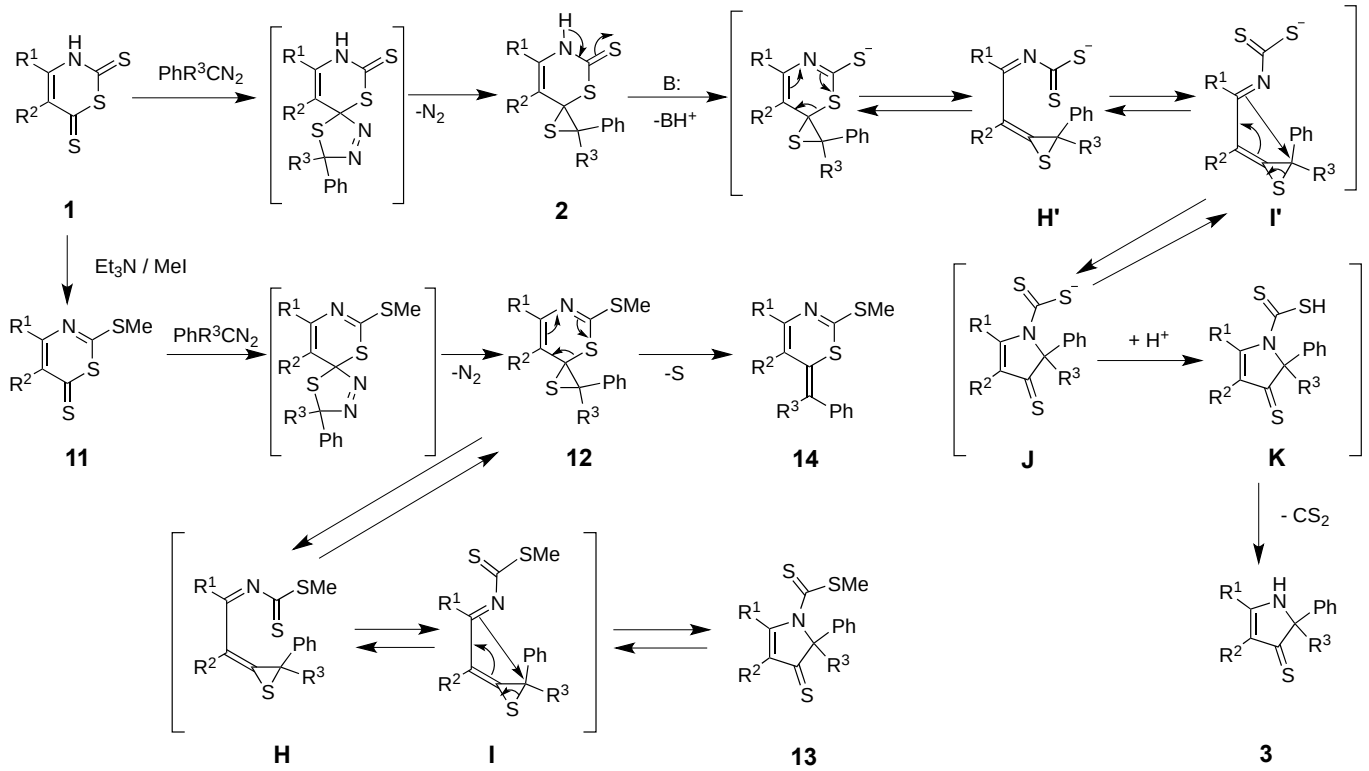
For example, the heat of formation for intermediate 2-phenyl-3-phenylsulfonyl-5,5-diphenyl-4-thioxopyrroline-1-dithiocarboxylate anion **C**, which was formed via the rearrangement of transient acyclic dithiocarboxylate anion **B**, was estimated to be 32.4 kcal/mol and that for the anion **A** of the reactant thiirane derivative **2a** was estimated to be 41.7 kcal/mol. As a result, the heat of reaction in this rearrangement is estimated to be $-\Delta H$ = 9.3 kcal, which means that the rearrangement of compound **2a** to pyrroline derivative **3a** is exothermic and the rearrengment proceeds smoothly.

On the other hand, similar calculation revealed that the heat of formation of the intermediate 3-ethoxycarbonyl-2-*p*-tolyl-4-thioxo-2-pyrroline-1-dithiocarboxylate anion **F** through transient acyclic dithiocarboxylate anion **E** and that for 5-ethoxycarbonyl-5,5-diphenyl-2-*p*-tolyl-1,3*(6H)*-thiazine-6-spiro-2-thiolate anion **D**, are very close. Accordingly, the heat of reaction for this rearrangement from

1,3(6*H*)-thiazine-6-spiro-2'-thiirane-2-thiolate anion **D** to the pyrroline-1-dithiocarboxylate anion **F** was estimated to be -*ΔH* = 1.2 kcal. Consequently, 1,3(6*H*)-thiazine-6-spiro-2'-thiirane derivative **2d** did not yield expected pyrroline derivative but produced desulfurized ethyl 6-diphenylmethylene-2-thioxo-1,3(6*H*)-thiazine-5-carboxylate **4** in quantitative yield in the presence of sodium 1,1-dimethylethoxide.

In addition, the calculated heat of reactions of the pyrroline derivatives **13a**,**b**,**e** produced by the rearrangement were estimated to be -*ΔH* = 2.6~9.7 kcal. These results point out that the pyrroline-4-thione derivatives **13a**,**b**,**e** by this rearrangement are all exothermic. The calculation results mentioned above suggest that the formation of pyrroline-4-thione derivatives **13a**,**b**,**e** are formed in high yields. The pirrolinethiones **13a**,**b**,**e** were really obtained in high to quantitative yields.

To the contrary, compared with each calculated heat of formation for 1,3(6*H*)-thiazine-6-spiro-2'-thiiranes **12c**,**d**, those for pyrroline derivatives **13c**,**d** were estimated to be high by 6.5~7.3 kcal/mol. These calculation results point out that these rearrengements are both endothermic and heating at high temperature for a long time in toluene is needed to form corresponding pyrroline derivatrives **13c**,**d**. Due to the drastic thermal condition, desulfurized products **14c**,**d** were also formed as by-products.



Scheme 8

The rearrangement process that leads to the formation of pyrroline derivatives **3** and **13**, starting with the reaction of 1,3-thiazine-2,6-dithiones or 2-methylthio-1,3-thiazine-6-thiones with higher analogs of

diazomethane, is expected to occur as follows: During the rearrangement of 2-methylthiothiazine-6-spirothiiranes **12** into methyl 4-thioxopyrroline-1-dithiocarboxylate derivatives **13**, the 6-spirothiiranes **12** would first open the thiazine ring by reversible electrocyclic reaction to form acyclic intermediates **H**, which convert to isomeric intermediates **I**. Subsequent rearrangement of acyclic intermediates **I** would lead to methyl 4-thioxopyrroline-1-dithiocarboxylates by [1,5]sigmatropy of the intermediates **I**.

On the other hand, in the rearrangement of 1,3-thiazine-6-spiro-2'-thiirane-2-thiones **2** to the pyrrolinethiones **3**, similar stepwise openings of both thiazine and thiirane rings would take place via electrocyclic reaction and would result in [1,5]sigmatropy of the ene-thiolate anions formed by a base. The generated intermediates **J** are neutralized to form dithiocarbamic acids **K** on acidification of the reaction mixture. The intermediates **K** are very unstable and dedithiocarboxylate swiftly to give *N*-unsubstituted pyrrolines **3** (**Scheme 8**).

EXPERIMENTAL

Mps were measured on a METTLER FP62 automatic melting point measurement apparatus and are uncorrected. NMR spectra were determined with a JEOL JNM-GX270-FT spectrometer at 270 MHz with tetramethylsilane as internal standard. IR spectra were determined with a JASCO FT-IR-5300 fourier transfer infrared spectrometer. UV and visible spectra were obtained on a Shimadzu UV-3100S UV-Vis recording spectrophotometer. All solvents used for each reaction and eluents for column chromatography were dried and distilled before use.

Starting Materials. 1,3-Thiazine-2,6-dithiones **1** and 3-substituted 1,3-thiazine-2,6-dithiones **8** were prepared by the reported method of synthesis by us.[1-3] 2-Methylthio-1,3-thiazine-6-thiones **11** were prepared by methylation of compounds **1** with iodomethane.[4]

Diphenyldiazomethane was prepared by usual method (oxidation of hydrazones by HgO)[17] and 1-phenyldiazoethane was prepared by applying the synthesis of phenyldiazomethane.[18]

The concentration of phenyldiazoethane was determined by back titration.[19]

3',3'-Diphenyl-5-phenylsulfonyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-2-thiones (2); To a solution of each 5-arylsulfonyl-1,3-thiazine-2,6-dithione (**1a-c**) (1 mmol) in THF (50 mL), was added dropwise a solution of diphenyldiazomethane (0.291 g, 1.5 mmol) in THF (5 mL) at room temperature. After 1 h, the reaction mixture was evaporated to dryness and then was added Et_2O (50 mL). The resulting solid was collected, dried, and recrystallized from each mixed solvent in parentheses after each mp.

4,3',3'-Triphenyl-5-phenylsulfonyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-2-thione (2a); Yield 70%. Mp 201.5-202.0 °C (CH_2Cl_2-hexane). δ_H (DMSO-d_6) 13.00 (s, br, 1H, NH) and 7.50-7.20 ppm (m, 20H, Ph×4). δ_C (DMSO-d_6) 197.4, 152.6, 140.9, 138.9, 137.7, 132.8, 132.4, 132.1, 129.1, 129.0, 128.5, 128.0, 127.9, 127.66, 125.7, 116.1, 67.5, and 51.0 ppm. ν_{max} (KBr) 3207 (NH), 3059, 2918, 1604, 1468, 1447,

1309 and 1141 (SO_2), 1257, 1179, 1074, 1037, 1024, 1001, 970, 941, 760, 727, 704, 667, 652, 629, and 500 cm^{-1}. (Found: C, 63.79; H, 3.66; N, 2.58; S, 23.70. $C_{29}H_{21}NO_2S_4$ requires C, 64.06; H, 3.89; N, 2.58; S, 23.59%)

4,3',3'-Triphenyl-5-*p*-tolylsulfonyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-2-thione (2b); Yield 67%. Mp 205.5 °C (DMSO-H_2O). δ_H (DMSO-d_6) 12.96 (s, br, 1H, NH), 7.5-7.1 (m, 14H, Ar), and 2.31 ppm (s, 3H, CH_3). δ_C (DMSO-d_6) 197.30, 169.3, 152.8, 152.3, 143.3, 143.0, 139.5, 138.9, 138.1, 138.0, 137.8, 137.6, 133.0, 132.5, 131.0, 130.8, 129.0, 128.9, 128.8, 128.0, 127.9, 127.8, 127.7, 127.6, 116.4, 114.3, 67.5, 54.7, 51.1, 50.3, and 20.9 ppm. ν_{max} (KBr) 3258 (NH), 3059, 2917, 1595, 1491, 1462, 1302, and 1142 (SO_2), 1258, 1074, 1022, 941, 758, 700, 665, 605, 557, and 530 cm^{-1}. (Found: C, 64.68; H, 4.09; N, 2.52; S, 23.18. $C_{30}H_{23}NO_2S_4$ requires C, 64.97; H, 4.16; N, 2.51; S, 22.99%)

3',3'-Diphenyl-4-*p*-tolyl-5-*p*-tolylsulfonyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-2-thione (2c); Yield 80%. Mp 207.0 °C (DMSO-H_2O) δ_H (DMSO-d_6) 12.88 (s, br, 1H, NH), 7.5-7.1 (m, 18H, Ar), 2.35 (s, 3H, CH_3), and 2.31 ppm (s, 3H, CH_3). δ_C (DMSO-d_6) 197.4, 169.4, 152.4, 143.3, 141.2, 138.9, 138.0, 137.6, 129.6, 129.0, 128.9, 128.8, 128.4, 127.9, 127.8, 127.6, 127.5, 115.9, 67.5, 54.7, 51.1, 20.91, and 20.8.8 ppm. ν_{max} (KBr) 3260 (NH), 3055, 3030, 2917, 1595, 1491, 1456, 1444, 1300, and 1140 (SO_2), 1256, 1184, 1074, 1037, 1020, 941, 810, 775, 743, 704, 664, 604, 556, and 530 cm^{-1}. (Found: C, 65.05; H, 4.42; N, 2.46; S, 22.17. $C_{31}H_{25}NO_2S_4$ requires C, 65.12; H, 4.41; N, 2.45; S, 22.43%)

3-Arylsulfonyl-5,5-diphenylpyrroline-4-thiones (3); A mixture of each 5-arylsulfonyl-3',3'-diphenyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-2-thione **2** (1 mmol), sodium 1,1-dimethylpropoxide (0.220 g, 2 mmol), and THF or DMF (80 mL) was warmed at 60 °C for 3 h. Water (150 mL) was added to the reaction mixture, and the resulting aqueous solution was acidified by adding 2 M-HCl at 0 °C. The resulting solid was collected, dried, and recrystallized from each mixed solvent in parentheses next each mp.

2,5,5-Triphenyl-3-phenylsulfonylpyrroline-4-thione (3a); Yield 61%. Mp 209.0-209.5 °C (DMF-EtOH-H_2O). δ_H (DMSO-d_6) 12.00 (s, br, 1H, NH) and 7.85-7.10 ppm (m, 20H, Ph×4). δ_C (DMSO-d_6) 217.2, 174.2, 141.8, 139.7, 132.6, 131.3, 129.2, 128.6, 128.3, 128.2, 128.1, 128.0, 127.8, 127.0, 125.0, and 86.2 ppm. ν_{max} (KBr) 3207 (NH), 3059, 2879, 1535, 1489, 1458, 1418, 1352, 1307, and 1144 (SO_2), 1277, 1204, 1078, 1024, 999, 758, 735, 694, 623, 589, 557, and 532 cm^{-1}. (Found: C, 71.62; H, 4.53; N, 2.94; S, 13.70. $C_{29}H_{21}NO_2S_2$ requires C, 71.92; H, 4.53; N, 3.00; S, 13.72%)

2,5,5-Triphenyl-3-*p*-tolylsulfonylpyrroline-4-thione (3b); Yield 67%. Mp 226.5 °C (acetone-hexane). δ_H (DMSO-d_6) 12.07 (s, br, 1H, NH), 7.73, 7.60, 7.31, and 7.20 (each m, 4+3+8+4H, Ph×3+tolyl) and 2.33 ppm (s, 3H, CH_3). δ_C (DMSO-d_6) 217.0, 174.1, 142.9, 139.8, 139.0, 131.3, 129.2, 128.8, 128.6, 128.1, 128.0, 127.8, 127.1, 125.2, 86.1, and 20.9 ppm. ν_{max} (KBr) 3190 (NH), 3059, 1541,

1491, 1451, 1412, 1354, 1315, and 1146 (SO_2), 1277, 1206, 1082, 1026, 914, 818, 756, 693, 610, 584, 544, and 532 cm^{-1}. (Found: C, 72.05; H, 4.83; N, 2.65; S, 13.13. $C_{29}H_{23}NO_2S_2$ requires C, 72.32; H, 4.81; N, 2.91; S, 13.32%)

5,5-Diphenyl-2-*p*-tolyl-3-*p*-tolylsulfonylpyrroline-4-thione (3c); Yield 67%. Mp 225.0 °C (acetone-hexane). δ_H (DMSO-d_6) 11.95 (s, br, 1H, NH), 7.71, 7.61, 7.36, (each d, each 2H, *J*= all 8 Hz, tolyl×2), 7.39 and 7.16 (each m, 10+4H, Ph×2+tolyl), 2.42 (s, 3H, CH_3), and 2.36 ppm (s, 3H, CH_3). δ_C (DMSO-d_6) 2168, 174.1, 142.9, 141.6, 139.8, 139.0, 128.7, 128.3, 128.1, 127.9, 127.8, 127.1, 126.2, 125.0, 85.9, 21.0, and 20.9 ppm. ν_{max} (KBr) 3200 (NH), 3026, 1543, 1498, 1448, 1354, 1299, and 1141 (SO_2), 1201, 1078, 1018, 816, 766, 698, 671, 607, 546, and 527 cm^{-1}. (Found: C, 72.43; H, 5.11; N, 2.06; S, 12.73. $C_{30}H_{25}NO_2S_2$ requires C, 72.70; H, 5.08; N, 2.83; S, 12.94%)

Formation of 6-Spiro-2'-thiirane-5-carboxylate (2d), **Ethyl 6-Diphenylmethylidene-2-thioxo-4-*p*-tolyl-1,3-thiazine-5-carboxylate (4), and Ethyl 2-Diphenylmethylthio-6-thioxo-4-*p*-tolyl-1,3-thiazine-5-carboxylate (5a) by the Reaction of Ethyl 2,6-Dithioxo-4-*p*-tolyl-1,3-thiazine-5-carboxylate (1d) with Diphenyldiazomethane.** To a solution of ethyl 2,6-dithioxo-4-*p*-tolyl-1,3-thiazine-5-carboxylate (**1d**) (0.323 g, 1 mmol) in THF (10 mL), a solution of diphenyldiazomethane (0.291 g, 1.5 mmol) in THF (10 mL) was added at room temperature. After 10 min, the solvent was removed under reduced pressure and the residue was column chromatographed (silica gel 60, 400 mesh, EtOAc : pentane = 1 : 20). Resulting each eluate was evaporated to dryness and each residue was washed with EtOH. **Ethyl 3',3'-triphenyl-2-thioxo-4-*p*-tolyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-5-carboxylate (2d)** (0.166 g, 34%), **ethyl 6-diphenylmethylidene-2-thioxo-4-*p*-tolyl-1,3-thiazine-5-carboxylate (4)** (0.133 g, 29%), and **ethyl 2-diphenylmethylthio-6-thioxo-4-*p*-tolyl-1,3-thiazine-5-carboxylate (5a)** (0.059 g, 12%) were isolated respectively.

Ethyl 3',3'-Triphenyl-2-thioxo-4-*p*-tolyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-5-carboxylate (2d); Yield 34%. Mp 219.0-220.0 °C (C_6H_6-hexane). δ_H ($CDCl_3$) 9.05 (s, br, 1H, NH), 7.5-7.2 (m, 14H, Ar), 3.64 (q, 1H, *J*=8 Hz, OCH_2), and 3.57 (q, 1H, *J*=8 Hz, OCH_2), 2.37 (s, 3H, CH_3), 0.73 ppm (t, 3H, *J*=8 Hz, CH_3). δ_C ($CDCl_3$) 196.9, 164.2, 144.3, 144.1, 143.7, 141.0, 140.2, 139.9, 139.0, 138.9, 131.3, 130.2, 129.6, 129.2, 128.9, 128.4, 128.2, 128.1, 128.0, 127.9, 111.6, 68.8, 61.0, 60.7, 56.6, 21.4, and 13.5 ppm. ν_{max} (KBr) 3234 (NH), 3052, 3021, 2988, 2923, 1696 (COO), 1631, 1508, 1473, 1445, 1369, 1318, 1309, 1273, 1249, 1220, 1180, 1094, 1044, 1020, 825, 768, 746, 700, 615, 564, and 532 cm^{-1}. UV-Vis λ_{max} (EtOH) 225.4 (log ε 4.38), 252.8 (4.15), 333.6 (4.08), and 295.2 nm (3.22) (Found: C, 66.10; H, 4.83; N, 2.87; S, 19.70. $C_{27}H_{23}NO_2S_3$ requires C, 66.23; H, 4.73; N, 2.86; S, 19.64%)

Ethyl 6-Diphenylmethylidene-2-thioxo-4-*p*-tolyl-1,3(6*H*)-thiazine-5-carboxylate (4); Yield 29%. Mp 227.0-228.0 °C (CH_2Cl_2-hexane). δ_H ($CDCl_3$)12.38 (s, br, 1H, NH), 7.44 (d, 4H, *J*=7 Hz, Ph-2,6×2),

7.3-7.1 (m, 10H, Ar), 3.06 (q, 2H, *J*=8 Hz, OCH_2), 2.32 (s, 3H, CH_3), and 0.61 ppm (t, 3H, *J*=8 Hz, CH_3). δ_C ($CDCl_3$) 191.3, 163.9, 144.8, 142.0, 139.1, 138.5, 130.4, 1299.9, 129.5, 128.8, 128.6, 128.4, 128.0, 127.8, 127.7, 120.3, 111.9, 59.9, 20.9, and 13.1 ppm. ν_{max} 3164 (NH), 3080, 2987, 2932, 1714 (COO), 1623, 1510, 1484, 1441, 1365, 1305, 1284, 1260, 1199, 1149, 1104, 1052, 1025, 973, 906, 831, 775, 762, 728, 697, 623, and 578 cm^{-1}. UV-Vis λ_{max} (EtOH) 255.8 (log ε 4.25), 293.6 (4.36), 325.6 (4.28), and 380.0 nm (3.73). (Found: C, 70.08; H, 5.08; N, 2.98; S, 14.32. $C_{26}H_{23}NO_2S_2$ requires C, 70.08; H, 5.20; N, 3.14; S, 14.39%)

Ethyl 2-Diphenylmethylthio-6-thioxo-4-*p*-tolyl-1,3(6*H*)-thiazine-5-carboxylate (5a); Yield 12%. Mp 239.5-240.5 °C (C_6H_6-hexane). δ_H (DMSO-d_6) 7.50 (d, 4H, *J*=7 Hz, Ph-2,6×2), 7.39 (t, 4H, *J*=7 Hz, Ph-3,5×2), 7.24 (d, 2H, *J*=8 Hz, *p*-tolyl-2,6), 7.20 (d, 2H, *J*=8 Hz, *p*-tolyl-3,5), 6.49 (s, 1H, $CHPh_2$), 4.10 (q, 2H, *J*=7 Hz, OCH_2), 2.35 (s, 3H, CH_3), and 1.06 ppm (t, 3H, *J*=7 Hz, CH_3). δ_C (DMSO-d_6) 199.9, 176.1, 166.4, 150.3, 141.7, 138.8, 133.5, 129.1, 128.8, 128.6, 128.0, 127.8, 126.9, 61.6, 54.3, 20.9, and 13.4 ppm. ν_{max} (KBr) 3026, 2978, 2921, 2855, 1719 (COO), 1838, 1609, 1521, 1509, 1459, 1340, 1254, 1230, 1188, 1098, 1061, 1011, 952, 857, 839, 748, 727, 698, 629, and 421 cm^{-1}. UV-Vis λ_{max} (EtOH) 266.8 (log ε 4.23), 324.0, (4.29), and 440.0 nm (3.93). (Found: C, 66.57; H, 4.74; N, 2.82; S, 19.94. $C_{27}H_{23}NO_2S_3$ requires C, 66.23; H, 4.73; N, 2.86; S, 19.64%)

Thermal Decomposition of Ethyl 3',3'-Triphenyl-2-thioxo-4-*p*-tolyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-5-carboxylate (2d). A mixture of ethyl 3',3'-triphenyl-2-thioxo-4-*p*-tolyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-5-carboxylate (**2d**) (0.244 g, 0.5 mmol), sodium 1,1-dimethylpropoxide (0.110 g, 1 mmol), and THF (40 mL) was heated at 60 °C for 24 h. Water (100 mL) was added to separate **ethyl 6-diphenylmethylidene-2-thioxo-4-*p*-tolyl-1,3-thiazine-5-carboxylate (4)** in 99% (0.226 g) yield.

Reaction of 2,6-Dithioxo-4-*p*-tolyl-1,3-thiazine-5-carbonitrile (1e) with Diphenyldizaomethane. To the THF (10 mL) solution of 5-cyano-4-*p*-tolyl-1,3-thiazine-2,6-dithione (**1e**, 0.276 g, 1 mmol) in THF (10 mL), was added a (THF) solution of diphenyldiazomethane (0.291 g, 1.5 mmol) in THF (10 mL) at 0 °C. After the reaction mixture was allowed to stand at 0 °C for 90 min, the solvent was removed under reduced pressure and then the residue was subjected to column chromatography (silica gel 60, 400 mesh, EtOAc : pentane = 1 : 20). Resulting each eluate was (were) evaporated to dryness, and (then) washed with (by) EtOH to give **2-diphenylmethylthio-1,3-thiazine-6-thione (5b)** and **two kinds of spiro-2'-thiiranes** (**6**) and (**7**). Physical and each spectral data for compounds **5b**, **6** and **7** were as follows: **2-Diphenylmethylthio-6-thioxo-4-*p*-tolyl-1,3-thiazine-5-carbonitrile (5b);** Yield 37% (0.164 g). Mp 91.5-92.0 °C (EtOH). δ_H ($CDCl_3$) 7.5-7.2 (m, 14H, Ar), 6.38 (s, 1H, CH), and 2.41 ppm (s, 3H, CH_3). δ_C ($CDCl_3$) 198.8, 179.1, 159.1, 143.8, 138.2, 132.7, 130.2, 129.7, 129.3, 129.0, 128.7, 128.5, 128.3, 128.2, 115.4, 107.7, 55.9, and 21.8 ppm. ν_{max} (KBr) 3058, 3026, 2978, 2917, 2214 (CN), 1605,

1490, 1432, 1401, 1340, 1245, 1185, 1147, 1078, 1031, 947, 824, 764, 747, 698, 627, 586, and 546 cm^{-1}. UV-Vis λ_{max} (EtOH) 250.0 (log ε 4.11), 250.0 (4.11), 282.4 (4.12), 312.8 (4.16), and 429.6 nm (3.54). (Found: C, 67.55; H, 4.12; N, 6.11; S, 21.56. $C_{25}H_{18}N_2S_3$ requires C, 67.84; H, 4.10; N, 6.33; S, 21.73%)

3',3'-Diphenyl-3-diphenylmethyl-2-thioxo-4-*p*-tolyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-5-carbonitrile (6); Yield 10% (0.060 g). Mp 168.5 °C (EtOH). δ_H ($CDCl_3$) 7.5-7.2 (m, 24H, Ar), 6.72 (s, 1H, CH), and 2.22 ppm (s, 3H, CH_3). δ_C ($CDCl_3$) 194.1, 158.8, 141.4, 137.9, 137.1, 136.2, 130.3, 130.3, 129.9, 129.8, 129.2, 128.5, 128.3, 128.1, 128.0, 127.9, 127.7, 127.2, 127.0, 115.8, 71.7, 67.9, 51.8, and 21.4 ppm. ν_{max} (KBr) 3061, 3022, 2922, 2217 (CN), 1591, 1556, 1492, 1454, 1443, 1323, 1284, 1255, 1226, 1182, 1148, 1077, 1052, 1031, 1017, 1000, 937, 904, 819, 766, 743, 716, 698, 630, 617, 607, and 592 cm^{-1}. UV-Vis λ_{max} (EtOH) 250.0 (log ε 4.11), 282.4 (4.12), 312.8 (4.16), and 429.6 nm (3.54). (Found: C, 75.09; H, 4.78; N, 4.52; S, 15.62. $C_{38}H_{28}N_2S_3$ requires C, 74.96; H, 4.64; N, 4.60; S, 15.80%)

3',3'-Diphenyl-2-diphenylmethylthio-4-*p*-tolyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-5-carbonitrile (7); Yield 30% (0.182 g). Mp 104.0-105.0 °C (EtOH). δ_H ($CDCl_3$) 7.1-7.5 (m, 24H, Ar), 6.35 (s, 1H, CH), and 2.24 ppm (s, 3H, CH_3). δ_C ($CDCl_3$) 168.6, 165.0, 159.4, 158.3, 146.3, 140.7, 140.6, 139.5, 139.4, 139.1, 137.9, 137.7, 133.1, 130.7, 130.4, 129.7, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 116.6, 116.5, 116.4, 93.4, 39.0, 69.6, 54.7, 53.2, and 21.5 ppm. ν_{max} (KBr) 3056, 3025, 2920, 2851, 2207 (CN), 1608, 1509, 1492, 1445, 1319, 1302, 1184, 1104, 1077, 1030, 984, 960, 900, 824, 747, 699, 632, 586, 367, and 352 cm^{-1}. UV-Vis λ_{max} (EtOH) 253.4 (log ε 4.25), 303.0 (4.30), and 409.6 nm (3.72). (Found: C, 75.19; H, 4.70; N, 4.70; S, 15.56. $C_{38}H_{28}N_2S_3$ requires C, 74.96; H, 4.64; N, 4.60; S, 15.80%)

Reaction of 2-Diphenylmethylthio-6-thioxo-4-*p*-tolyl-1,3-thiazine-5-carbonitrile (5b) with Diphenyldiazomethane. To the THF (10 mL) solution of 5-cyano-2-diphenylmethylthio-4-*p*-tolyl-1,3-thiazine-6-thione (**5**) (0.221 g, 0.5 mmol), a THF solution (10 mL) of diphenyldiazomethane (0.097 g, 0.5 mmol) was added at 0 °C. The reaction mixture was allowed to stand at 0 °C for 90 min. The solvent was removed at reduced pressure and then subjected to column chromatography (silica gel 60, 400 mesh, EtOAc : pentane = 1 : 20). **3',3'-Diphenyl-2-diphenylmethylthio-4-*p*-tolyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-5-carbonitrile (7)** was yielded in 15% (0.091 g).

3-Substituted 3',3'-Diphenyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-2-thiones (9); A mixture of each 3-substituted 1,3-thiazine-2,6-dithione **8** (1 mmol), diphenyldiazomethane (0.233 g, 1.2 mmol), and THF (50 mL) was allowed to stand for 1 h at room temprature. The solvent was removed at reduced pressure and then subjected to column chromatography (silica gel 60, 400 mesh, benzene) and recristallized from each mixed solvent in parentheses.

3,4-Dimethyl-3',3'-diphenyl--2-thioxo-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-5-carbonitrile (9a); Yield

98%. Mp 243.0-246.5 °C (CH_2Cl_2-hexane). δ_H ($CDCl_3$) 7.4-7.2 (m, 10H, Ph×2), 3.83 (s, 3H, N-CH_3), and 2.36 (s, 3H, CH_3) ppm. δ_C ($CDCl_3$) 196.6, 153.7, 138.3, 129.7, 129.5, 129.1, 128.9, 128.7, 128.5, 128.4, 128.3, 128.2, 115.3, 99.1, 68.6, 51.4, 39.1, and 21.2 ppm. ν_{max} (KBr) 2209 (CN), 1603, 1447, 1383, 1331, 1277, 1169, 1103, 1005, 822, 770, 747, 704, and 644 cm^{-1}. UV-Vis λ_{max} (EtOH) 228.5 (log ε 4.06), 262.5 (3.20), 334.5 (4.13), and 403.5 nm (2.94). (Found: C, 63.28; H, 4.33; N, 7.25; S, 25.61. $C_{20}H_{16}N_2S_3$ requires C, 63.12; H, 4.24; N, 7.35; S, 25.28%)

3-Methyl-4,3',3'-triphenyl-2-thioxo-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-5-carbonitrile (9b); Yield 89%. Mp 255.0-261.0 °C (CH_2Cl_2-hexane). δ_H ($CDCl_3$) 7.5-7.3 (m, 15H, Ph×3) and 3.51 ppm (s, 3H, NCH_3). δ_C ($CDCl_3$) 197.0, 156.3, 138.1, 137.8, 132.2, 131.4, 129.8, 129.3, 128.8, 128.6, 128.3, 127.9, 115.5, 99.7, 68.5, 51.5, and 42.5 ppm. ν_{max} (KBr) 2216 (CN), 1593, 1489, 1445, 1426, 1331, 1290, 1263, 1231, 1198, 1113, 1080, 1053, 1028, 1001, 976, 928, 895, 847, 785, 774, 750, 704, and 675cm^{-1}. UV-Vis λ_{max} (EtOH) 230.0 (log ε 4.12), 263.0 (3.95), 338.5 (4.09), and 418.0 nm (3.49). (Found: C, 67.87; H, 4.27; N, 6.18; S, 21.55. $C_{25}H_{18}N_2S_3$ requires C, 67.84; H, 4.10; N, 6.33; S, 21.73%)

3-Methyl-3',3'-diphenyl-2-thioxo-4-*p*-tolyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-5-carbonitrile (9c); Yield 93%. Mp 289.0 °C (CH_2Cl_2-hexane). δ_H ($CDCl_3$) 7.5-7.2 (m, 14H, Ar), 3.50 (s, 3H, NCH_3), and 2.33 ppm (s, 3H, CH_3). δ_C ($CDCl_3$) 196.9, 156.5, 141.8, 138.1, 137.8, 130.4, 129.7, 129.4, 129.1, 128.9, 128.7, 128.5, 128.2, 127.8, 115.6, 99.2, 68.5, 51.5, 42.6, and 21.5 ppm. ν_{max} (KBr) 2216 (CN), 1591, 1560, 1508, 1491, 1458, 1442, 1340, 1313, 1294, 1265, 1219, 1186, 1157, 1109, 1076, 1020, 993, 939, 846, 819, 769, 735, 700, and 669 cm^{-1}. UV-Vis λ_{max} (EtOH) 229.0 (log ε 4.15), 272.5 (4.01), 338.5 (4.14), and 422.0 nm (3.41). (Found: C, 68.10; H, 4.28; N, 5.86; S, 20.88. $C_{26}H_{20}N_2S_3$ requires C, 668.39; H, 4.41; N, 6.13; S, 21.06%)

Ethyl 3,4,3',3'-Tetraphenyl-2-thioxo-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-5-carboxilate (9d); Yield 71%. Mp 156.0-158.0 °C (CH_2Cl_2-hexane). δ_H ($CDCl_3$) 7.57 (d, 2H, *J*=7 Hz, NPh-*o*), 7.53 (d, 2H, *J*=7 Hz, 3-Ph-o), 7.4-6.9 (m, 16H, Ph×4), 3.40 and 3.37 (each q, each 1H, *J*=7 Hz, OCH_2), and 0.55 (t, 3H, *J*=7 Hz, CH_3) ppm. δ_C ($CDCl_3$) 196.0, 164.1, 146.5, 139.9, 139.0, 133.4, 130.1, 129.8, 129.6, 128.9, 128.7, 128.5, 128.3, 127.7, 127.4, 119.7, 68.1, 60.8, 53.1, and 13.2 ppm. ν_{max} (KBr) 1714 (COO), 1624, 1591, 1543, 1489, 1444, 1367, 1311, 1275, 1213, 1178, 1086, 1016, 966, 922, 895, 856, 812, 750, 692, and 661 cm^{-1}. UV-Vis λ_{max} (EtOH) 232.5 (log ε 4.42), and 331.0 (4.09), 415.5 nm (2.83). (Found: C, 69.42; H, 4.76; N, 2.59; S, 17.23. $C_{32}H_{25}NO_2S_3$ requires C, 69.66; H, 4.57; N, 2.54; S, 17.43%)

Thermal Decomposition of *N*-Substituted 3',3'-Diphenyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-2-thiones (9); The ethylene glycolic solution (40 mL) of each 3-substituted 3',3'-diphenyl-1,3(6*H*)-thiazine- 6-spiro-2'-thiirane-2-thione **9** (1 mmol) was heated at 190 °C for 1 h. The resulting each solution was cooled to 0 °C to separate each solid. Each collected

6-diphenylmethylidene-1,3-thiazine-2-thiones (10) was washed with EtOH, dried, and recrystallized from each mixed solvent in parentheses.

3,4-Dimethyl-6-diphenylmethylidene-2-thioxo-1,3-thiazine-5-carbonitrile (10a); Yield 72%. Mp 250.0-151.0 ºC (CH_2Cl_2-hexane). δ_H ($CDCl_3$) 7.37 (m, 6H, Ph-*m,p*), 7.15 and 7.07 (each m, each 2H, Ph-*o*), 3.70 (s, 3H, NCH_3), and 2.45 (s, 3H, CH_3) ppm. δ_C ($CDCl_3$) 195.0, 152.0, 139.0, 138.9, 130.4, 129.2, 129.0, 128.5, 128.4, 115.8, 115.0, 97.8, 38.9, and 20.5 ppm. ν_{max} (KBr) 2212 (CN), 1560, 1491, 1429, 1379, 1340, 1315, 1300, 1277, 1192, 1105, 1059, 1006, 953, 923, 856, 771, 754, 704, and 627 cm^{-1}. UV-Vis λ_{max} (EtOH) 232.5 (log ε 3.79), 260.5 (4.03), 301.0 (4.32), 325.0 (3.70), and 375.0 nm (4.26). (Found: C, 68.75; H, 4.69; N, 7.83; S, 18.11. $C_{20}H_{16}N_2S_2$ requires C, 68.93; H, 4.63; N, 8.04; S, 18.40%)

3-Methyl-4-phenyl-6-diphenylmethylidene-2-thioxo-1,3-thiazine-5-carbonitrile (10b); Yield 71% Mp 263.0-267.0 ºC (CH_2Cl_2-hexane). δ_H ($CDCl_3$) 7.5-7.3 (m, 11H, Ph), 7.27 (m, 2H, Ph-*o*), and 3.36 ppm (s, 3H, NCH_3). δ_C ($CDCl_3$) 195.2, 154.5, 144.6, 139.1, 138.8, 132.4, 131.1, 130.9, 130.4, 130.1, 129.3, 129.1, 128.9, 128.6, 128.4, 116.0, 114.8, 98.9, and 42.4 ppm. ν_{max} (KBr) 2214 (CN), 1591, 1556, 1487, 1456, 1342, 1294, 1271, 1157, 1109, 1026, 991, 931, 841, 769, 698, 667, and 642 cm^{-1}. UV-Vis λ_{max} (EtOH) 235.0 (log ε 4.07), 262.5 (4.24), 306.5 (4.32), and 374.5 nm (3.77). (Found: C, 72.34; H, 4.56; N, 6.74; S, 15.21. $C_{25}H_{18}N_2S_2$ requires C, 73.14; H, 4.42; N, 6.82; S, 15.40%)

3-Methyl-6-diphenylmethylidene-4-*p*-tolyl-2-thioxo-1,3-thiazine-5-carbonitrile (10c); Yield 97%. Mp 296.0-298.0 ºC (CH_2Cl_2-hexane). δ_H ($CDCl_3$) 7.5-7.4 (m, 6H, Ar), 7.4-7.2 (m, 6H, Ar), 7.10 (m, 2H, Ar), 3.38 (s, 3H, NCH_3), and 2.40 ppm (s, 3H, CH_3) ppm. δ_C ($CDCl_3$) 195.3, 154.8, 144.5, 141.7, 139.2, 138.8, 130.5, 130.1, 130.0, 129.4, 129.3, 129.1, 128.8, 128.6, 128.4, 116.2, 115.0, 98.6, 42.5, and 21.5 ppm. ν_{max} (KBr) 2216 (CN), 1591, 1560, 1508, 1491, 1458, 340, 1313, 1294, 1265, 1219, 1186, 1157, 1109, 1076, 993, 339, 819, 769, 733, 700, and 669 cm^{-1}. UV-Vis λ_{max} (EtOH) 230.0 (log ε 4.04), 265.0 (4.15), 302.0 (4.30), and 377.5 nm (3.71). (Found: C, 73.56; H, 4.59; N, 6.42; S, 15.22. $C_{26}H_{20}N_2S_2$ requires C, 73.55; H, 4.75; N, 6.60; S, 15.10%)

Ethyl 3,4-Diphenyl-6--diphenylmethylidene-2-thioxo-1,3-thiazine-5-carboxylate (10d); Yield 96%. Mp 189.0-189.5 ºC (CH_2Cl_2-hexane). δ_H ($CDCl_3$) 7.4-7.1 (m, 20H, Ph), 3.00 (q, 2H, *J*=7 Hz, OCH_2), and 0.55 (t, 3H, *J*=7 Hz, CH_3) ppm. δ_C ($CDCl_3$) 194.5, 164.9, 146.7, 144.1, 140.2, 139.7, 134.2, 130.08, 130.2, 129.0, 128.6, 128.4, 128.3, 128.2, 127.9, 127.3, 119.6, 118.9, 60.6, and 13.1 ppm. ν_{max} (KBr) 1713 (COO), 1589, 1489, 1443, 1366, 1327, 1288, 1232, 1190, 1153, 1089, 1030, 918, 843, 808, 768, 704, and 640 cm^{-1}. UV-Vis λ_{max} (EtOH) 301.0 nm (log ε 4.44). (Found: C, 74.16; H, 4.66; N, 2.53; S, 12.10. $C_{32}H_{25}NO_2S_2$ requires C, 73.96; H, 4.85; N, 2.70; S, 13.34%)

Formation of 1,3(6*H*)-Thiazine-6-spiro-2'-thiiranes (12) Except for the 6'-Spiro-2'-thiiranes 12b and 12g by the Reaction of 2-Methylthio-1,3-thiazine-6-thiones (11) with Diphenyldizaomethane.

5-Methylsulfonyl-2-methylthio-4,3',3'-triphenyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane (12a). To a solution of 2-methylthio-4-phenyl-5-methylsulfonyl-1,3-thiazine-6-thione (**11a**) (0.329 g, 1 mmol) in THF (10 mL), a solution of diphenyldiazomethane (0.291 g, 1.5 mmol) in THF (10 mL) was added at room temperature and was allowed to stand at room temperature for 1 h. The solvent of reaction mixture was removed under reduced pressure to dryness at 0 °C. The solid remained was column chromatographed (silica gel 60, 400 mesh, EtOAc : pentane = 1 : 10) at 0 °C. Yield 94% (0.465 g) (gradually decomposed during recrystallization). Mp 147.5-148.0 °C (benzene-hexane). δ_H ($CDCl_3$) ca. 7.2 (m, 15H, 3 × C_6H_5), 2.57 (s, 3H, SCH_3), and 2.36 ppm (s, 3H, SO_2CH_3). δ_C ($CDCl_3$) 176.8, 158.8, 138.4, 137.6, 130.8, 129.9, 129.4, 129.2, 128.3, 128.2, 128.0, 117.3, 68.7, 46.2, and 15.7 ppm. ν_{max} (KBr) 3057, 1926, 1520, 1487, 1450, 1302, and 1134 (SO_2), 1262, 1175, 1076, 992, 623, 891, 787, 756, 712, 629, 584, 561, 517, 450, 442, and 405 cm^{-1}. UV-Vis λ_{max} (EtOH) 230.5 (log ε 4.05), 299 (3.93), 400.5 (3.47), and 408.0 nm (3.48). (Found: C, 60.28; H, 4.37; N, 2.93; S, 25.60. $C_{25}H_{21}NO_2S_4$ requires C, 60.58; H, 4.27; N, 2.83; S, 25.87%)

2-Methylthio-4,3',3'-triphenyl-5-phenylsulfonyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane (12b); Comound **12b** was first obtained when the reaction was carried out at –50 °C. Thus, to a solution of 2-methylthio-4-phenylsulfonyl-1,3-thiazine-6-thione (**11b**) (0.391 g, 1 mmol) in THF (10 mL), a solution of diphenyldiazomethane (0.291 g, 1.5 mmol) in THF (10 mL) was added at –50 °C. The reaction mixture was allowed to stand at –50 °C for 2 h and then the solvent was removed thoroughly under reduced pressure at 0 °C. The remained solid was column chromatographed (silica gel 60, 400 mesh, EtOAc : pentane = 1 : 10) at 0 °C. Yield 71% (0.395 g) (gradually decomposed during recrystallization). Mp 135.0-135.5 °C. δ_H ($CDCl_3$) ca. 7.4 (m, 20H, 4 × C_6H_5) and 2.57 ppm (s, 3H, SCH_3). δ_C ($CDCl_3$) 76.0, 158.0, 141.4, 137.9, 137.3, 137.2, 136.8, 132.2, 130.1, 129.8, 129.6, 129.5, 128.7, 128.3, 128.0, 127.8, 127.8, 127.3, 117.3, 67.4, 51.1, and 15.8 ppm. ν_{max} (KBr) 3075, 3030, 2926, 1597, 1582, 1510, 1483, 1443, 1308, and 1144 (SO_2), 1265, 1172, 1082, 1034, 993, 968, 926, 909, 889, 843, 831, 787, 756, 725, 708, 693, 660, and 631 cm^{-1}. (Found: C, 63.98; H, 4.27; N, 2.24; S, 23.11. $C_{30}H_{23}NO_2S_4$ requires C, 64.60; H, 4.16; N, 2.51; S, 22.99%)

Ethyl 2-Methylthio-4,3',3'-triphenyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-5-carboxylate (12c): Compound **12c** was obtained and purified similarly to 5-methylsulfonyl-6-spiro-2'-thiirane **12a** Yield 96%. Mp 170 °C (dec.) (benzene-hexane). δ_H ($CDCl_3$) ca. 7.3 (m, 15H, 3 × C_6H_5), 3.51 and 3.49 (each q, each 1H, *J*=7.3 Hz, OCH_2), 2.54 (s, 3H, SCH_3), and 0.56 ppm (t, 3H, *J*=7.3 Hz, CH_3). δ_C ($CDCl_3$) 166.3, 165.8, 150.5, 139.0, 138.3, 130.0, 129.6, 128.6, 128.0, 127.9, 127.8, 127.5, 114.7, 69.6, 60.6, 54.0, 14.9, and 13.2 ppm. ν_{max} (KBr) 3057, 3022, 2980, 2920, 1705 (COO), 1582, 1559, 1530, 1491, 1464, 1445, 1392, 1368, 1319, 1308, 1285, 1240, 1221, 1175, 1067, 1030, 984, 939, 922, 893, and 862 cm^{-1}. UV-Vis

λ_{max} (EtOH) 220.5 (log ε 4.26), 235.0 (4.32), 279.5 (4.39), and 316.5 nm (4.20). (Found: C, 65.98; H, 4.83; N, 2.69; S, 19.55. $C_{27}H_{23}NO_2S_3$ requires C, 66.23; H, 4.73; N, 2.86; S, 19.64%).

2-Methylthio-3',3'-diphenyl-4-*m*-tolyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-5-carbonitrile (12d); Compound **12d** was also obtained and purified similarly to the 5-methylsulfonyl-6-spiro-2'-thiirane **12a.** Yield 70%. Mp 148 °C (dec.) (EtOAc-hexane). δ_H ($CDCl_3$) ca. 7.4 (m, 14H, Ar), 2064 (s, 3H, CH_3), and 2.37 ppm (s, 3H, SCH_3). δ_C ($CDCl_3$) 170.9, 159.5, 138.1, 137.8, 136.3, 131.3, 130.0, 129.1, 128.4, 128.3, 128.1, 128.0, 116.6, 21.4, and 15.2 ppm. ν_{max} (KBr) 3057, 3029, 2924, 2207 (CN), 1597, 1583, 1539, 1489, 1445, 1314, 1277, 1184, 1117, 1080, 1032, 985, 947, 922, 847, 797, 772, 745, 733, 702, 640, 613, 582, 565, and 513 cm^{-1}. UV-Vis λ_{max} (EtOH) 220.5 (log ε 4.68), 232.5 (4.61), and 292.5 (4.52), 355.0 nm (4.19). (Found: C, 68.39; H, 4.47; N, 6.10; S, 21.22. $C_{26}H_{20}N_2S_3$ requires C, 68.39; H, 4.41; N, 6.13; S, 21.07%)

3'-Methyl-5-methylsulfonyl-2-methylthio-4,3'-diphenyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane (12e); To a solution of 2-methylthio-5-methylsulfonyl-4-phenyl-1,3-thiazine-6-thione (**11a**) (0.329 g, 1 mmol) in THF (10 mL), was added a solution of 1-phenyldiazoethane (1.5 mmol) in THF (10 mL) at room temperature. The reaction mixture was allowed to stand at room temperature for 20 min. Then the solvent was removed under reduced pressure and was column chromatographed (silica gel 60, 400 mesh, EtOAc : pentane = 4 : 1). Yield 97% (0.480 g). Mp 114 °C (dec.)(benzene-hexane). δ_H ($CDCl_3$) 7.3-7.0 (m, 8H, 2×Ph), 6.88 (d, 2H, *J*=7 Hz, Ph-2,6), and 2.72 (s, 3H, SO_2CH_3), 2.49 (s, 3H, SCH_3), 2.00 ppm (s, 3H, CH_3). δ_C ($CDCl_3$)173.8, 158.4, 138.7, 138.1, 129.9, 129.4, 129.1, 128.4, 128.1, 127.9, 119.1, 59.8, 51.1, 46.5, 27.3, and 15.6 ppm. ν_{max} (KBr) 3029, 2959, 2924, 1601, 1520, 1487, 1458, 1375, and 1132 (SO_2), 1304, 1258, 1071, 1028, 1009, 961, 928, 897, 785, 756, 708, 644, and 613 cm^{-1}. UV-Vis λ_{max} (log ε) 210.5 (4.36), 292.5 (4.07), and 401.0 nm (3.42). (Found: C, 55.65; H, 4.56; N, 3.34; S, 29.30. $C_{20}H_{19}NO_2S_4$ requires C, 55.40; H, 4.42; N, 3.23; S, 29.58%)

Methyl 5-Methyl-2,5-diphenyl-3-phenylsulfonyl-4-thioxopyrroline-1-dithiocarboxylate (13f); Compound **13f** was obtained similarly to the formation of the 5-methylsulfonyl-6-spiro-2'-thiirane **12e** from the reactants, 2-methylthio-4-phenyl-5-phenylsulfonyl-1,3-thiazine-6-thione **11b** (0.391 g, 1 mmol) and 1-phenyldiazoethane (1.5 mmol). After the reaction mixture was allowed to stand at room temperature for 3 min, the solvent was removed under reduced pressure and column chromatographed (silica gel 60, 400 mesh, EtOAc : pentane = 1 : 10). Yield 82% (0.457 g). Mp 172.5-175.5 °C (benzene-hexane). δ_H ($CDCl_3$) ca. 7.5 (m, 15H, 3 × C_6H_5), 2.31(s, 3H, SCH_3), and 2.16ppm (s, 3H, CH_3). δ_C ($CDCl_3$) 221.7, 204.3, 173.5, 140.8, 139.0, 133.0, 131.5, 130.5, 129.5, 128.3, 128.2, 127.8, 127.7, 125.7, 88.4, 25.1, and 21.6 ppm. ν_{max} (KBr) 3061, 1601, 1582, 1508, 1447, 1387, 1335, 1273, and 1157 (SO_2), 1073, 1040, 928, 907, 858, 760, 747, 735, 714, 691, 662, and 637 cm^{-1}. UV-Vis λ_{max} (EtOH)

210.5 (log ε 4.49), 292.5 (4.12), 328.5 (3.94), 404.0 (4.34), and 478.0 nm (3.24). (Found: C, 60.39; H, 4.57; N, 2.83; S, 25.59. $C_{25}H_{21}NO_2S_4$ requires C, 60.58; H, 4.27; N, 2.83; S, 25.87%)

Thermal Rearrangement of 1,3(6*H*)-Thiazine-6-spiro-2'-thiiranes (12a-d) into Methyl 3-Methylsulfonyl-2,5,5-triphenylpyrroline-4-thioxo-1-dithiocarboxylate (13a). A solution of 2-methylthio-5-methylsulfonyl-4,3',3'-triphenyl-1,3-thiazine-6-spiro-2'-thiirane (**12a**) (0.248 g, 0.5 mmol) in toluene (50 mL) was refluxed at 110 °C for 4 min. The reaction mixture was evaporated to dryness and the residue was column chromatographed (silica gel 60, 400 mesh, EtOAc : pentane = 1 : 10). Yield 76% (0.376 g) (direct 0%). Mp 186.5-187.5 °C (benzene-hexane). δ_H ($CDCl_3$) ca. 7.5 (m, 15H, 3 × C_6H_5), 3.13 (s, 3H, SO_2CH_3), and 2.13 ppm (s, 3H, SCH_3). δ_C ($CDCl_3$) 223.1, 205.6, 173.3, 137.4, 131.9, 131.2, 129.9, 129.2, 128.9, 128.3, 128.0, 127.7, 96.2, 42.3, and 21.4 ppm. ν_{max} (KBr) 3057, 1516, 1470, 1364, 1318, and 1141 (SO_2), 1277, 1084, 1036, 999, 947, 880, 758, 739, 698, 584, 540, 515, 480, and 421 cm^{-1}. UV-Vis λ_{max} (EtOH) 249.0 (log ε 4.05), 409.0 (4.25), and 471.0 nm (3.08). (Found: C, 61.48; H, 4.49; N, 2.66; S, 25.65. $C_{25}H_{21}NO_2S_4$ requires C, 60.58; H, 4.27; N, 2.83; S, 25.87%). Compound **14a** was isolated together with compound **13a** as by-product; **5-Methylsulfonyl-2-methylthio-4-phenyl-6-diphenylmethylidene-1,3-thiazine (14a);** Yield 19%. Mp 168.5-169.0 °C (benzene-hexane). δ_H ($CDCl_3$) ca. 7.2 (m, 15H, 3 × C_6H_5), 2.51 (s, 3H, SCH_3), and 2.07 ppm (s, 3H, SO_2CH_3). δ_C ($CDCl_3$) 163.8, 162.3, 148.6, 140.6, 139.9, 134.0, 130.0, 129.8, 129.7, 129.3, 129.0, 128.4, 128.3, 128.2, 126.7, 125.0, 43.7, and 16.5 ppm. ν_{max} (KBr) 3032, 2926, 1532, 1485, 1443, 1314, and 1140 (SO_2), 1244, 1074, 1028, 964, 936, 883, 761, 702, 631, 613, 583, 559, 536, 494, 440, and 403 cm^{-1}. UV-Vis λ_{max} (EtOH) 241.0 (log ε 4.20), 285.0 (4.14), and 399.5 nm (3.05). (Found: C, 64.36; H, 4.31; N, 3.22; S, 20.87. $C_{25}H_{21}NO_2S_3$ requires C, 64.76; H, 4.57; N, 3.02; S, 20.75%)

Methyl 2,5,5-Triphenyl-3-phenylsulfonyl-4-thioxopyrroline-1-dithiocarboxylate (13b); A solution of 2-methylthio-4,3',3'-triphenyl-5-phenylsulfonyl-1,3-thiazine-6-spiro-2'-thiirane (**12b**) (0.278 g, 0.5 mmol) in benzene (50 mL) was allowed to stand at room temprature for 20 min. After being evaporated to dryness, the solid residue was column chromatographed (silica gel 60, 400 mesh, benzene). Yield 100% (0.278 g). Mp 188-190 °C (benzene-hexane). δ_H ($CDCl_3$) ca. 7.5 (m, 20H, 3 × C_6H_5) and 2.10 ppm (s, 3H, SCH_3). δ_C ($CDCl_3$) 221.8, 205.4, 173.4, 1403, 137.2, 132.6, 131.8, 130.7, 129.9, 129.8, 129.6, 128.6, 128.3, 128.0, 127.9, 127.8, 127.5, 96.1, and 21.3 ppm. ν_{max} (KBr) 3059, 2917, 1603, 1582, 1512, 1493, 1464, 1445, 1373, 1323, and 1151 (SO_2), 1285, 1250, 1127, 1082, 1036, 999, 965, 949, 914, 880, 795, 756, 737, and 716 cm^{-1}. UV-Vis λ_{max} (EtOH) 299.0 (log ε 4.12), 407.5 (4.28), and 487.0 nm (3.06). (Found: C, 64.84; H, 4.34; N, 2.51; S, 23.21. $C_{30}H_{23}NO_2S_4$ requires C, 64.60; H, 4.16; N, 2.51; S, 22.99%)

Direct Formation of Methyl 2,5,5-Triphenyl-3-phenylsulfonyl-4-thioxopyrroline-1-dithio-

carboxylate (13b). To a solution of 2-methylthio-4-phenyl-5-phenylsulfonyl-1,3-thiazine-6-thione (**11a**) (0.391 g, 1 mmol) in THF (10 mL), diphenyldiazomethane (0.291 g, 1.5 mmol) in THF (10 mL) was added at room temperature. The mixture was allowed to stand at room temperature for 20 min, then the solvent was removed under reduced pressure to dryness and the residue was column chromatographed (silica gel 60, 400 mesh, benzene). Yield 98% (0.546 g).

Ethyl 1-(Methylthio)thiocarbonyl-2,5,5-triphenyl-4-thioxo-3-carboxylate (13c); Compound **13c** was obtained similarly to compound **13a** from ethyl 2-methylthio-4,3',3'-triphenyl-1,3-thiazine-6-spiro-2'-thiirane-5-carboxylate (**12c**) (0.489 g, 1 mmol) by refluxing in toluene at 110 °C for 2 h and isolated similarly to the isolation of compound **13a**. Yield 69% (0.337 g). Mp 183.5-186.0 °C (EtoAc-hexane). δ_H ($CDCl_3$) ca. 7.5 (m, 15H, 3 × C_6H_5), 4.13 (q, 2H, *J*=7.0 Hz, OCH_2), 2.13 (s, 3H, SCH_3), and 1.03 ppm (t, 3H, *J*=7.0 Hz, CH_3). δ_C ($CDCl_3$) 225.0, 205.3, 170.3, 163.4, 137.9, 131.2, 131.0, 29.3, 129.0, 128.6, 128.5, 128.2, 128.1, 127.9, 127.6, 95.8, 61.1, 20.9, and 13.8 ppm. ν_{max} (KBr) 3063, 2992, 1726 (COO), 1553, 1491, 1445, 1404, 1296, 1213, 1154, 1032, 1017, 901, 768, 727, 696, and 602 cm^{-1}. UV-Vis λ_{max} (EtOH) 210.5 (log ε 4.55), 299.0 (4.14), and 417.5 nm (4.31). (Found: C, 66.00; H, 4.90; N, 2.90; S, 19.35. $C_{27}H_{23}NO_2S_3$ requires C, 66.23; H, 4.73; N, 2.86; S, 19.64%). Desulfurized compound, **ethyl 6-diphenylmethylidene-2-methylthio-4-phenyl-1,3-thiazine-5-carboxylate** (**14c**) was also isolated as by-product. Yield 25%. Mp 199.5-211.5 °C (benzene-hexane). δ_H ($CDCl_3$) ca. 7.3 (m, 15H, 3 × C_6H_5), 3.21 (q, 2H, *J*=6.5 Hz, OCH_2), 2.52 (s, 3H, SCH_3), and 0.66 ppm (t, 3H, *J*=6.5 Hz, CH_3). δ_C ($CDCl_3$) 167.5, 152.8, 146.0, 140.6, 140.2, 138.6, 131.2, 130.6, 128.7, 128.6, 128.3, 128.0, 127.8, 127.7, 115.7, 60.5, 14.6, and 13.1 ppm. ν_{max} (KBr) 3057, 2980, 2922, 1713 (COO), 1532, 1485, 1443, 1327, 1304, 1192, 1088, 1074, 1030, 988, 775, and 702 cm^{-1}. UV-Vis λ_{max} (EtOH) 210.5 (log ε 4.51), 254.5 (4.35), 287.5 (4.35), and 390.5 nm (3.78). (Found: C, 70.76; H, 5.19; N, 2.64; S, 13.87. $C_{27}H_{23}NO_2S_2$ requires C, 70.87; H, 5.07; N, 3.06; S, 14.01%)

Methyl 3-Cyano-5,5-diphenyl-4-thioxo-5-*m*-tolylpyrroline-1-dithiocarboxylate (13d); Compound **13d** was obtained similarly to compound **12a** from 2-methylthio-3',3'-diphenyl-4-*m*-tolyl-1,3-thiazine-6-spiro-2'-thiirane-5-carbonitrile (**12d**) (0.228 g, 0.5 mmol) by refluxing in toluene (50 mL) at 110 °C for 20 h and isolated similarly to the isolation of compound **13a**. Yield 41% (0.093 g). Mp 196.5-197.5 °C (EtOAc-hexane). δ_H ($CDCl_3$) ca. 7.74 (s, 1H, m-tolyl-2), 7.59-7.53 (m, 4H, Ar), 4.41-7.37 (m, 8H, Ar), 2.45 (s, 3H, CH_3), and 2.20 ppm (s, 3H, SCH_3). δ_C ($CDCl_3$) 224.5, 205.4, 174.2, 139.4, 137.2, 133.9, 133.6, 130.4, 129.8, 129.2, 129.0, 128.8, 128.7, 128.0, 127.2, 125.6, 114.2, 109.7, 96.4, 21.5, and 21.2 ppm. ν_{max} (KBr) 3048, 2945, 2228 (CN), 1584, 1530, 1491, 1476, 1443, 1375, 1293, 1263, 1148, 1130, 1036, 999, 959, 928, 899, 878, 849, 802, 781, 762, 741, 721, 710, 697, 675, 608, and 579 cm^{-1}. UV-Vis λ_{max} (EtOH) 302.5 (log ε 4.57) and 418.5 nm (4.71). (Found: C, 68.39; H, 4.55; N, 6.06; S, 21.11.

$C_{26}H_{20}N_2S_3$ requires C, 68.39; H, 4.41; N, 6.13; S, 21.06%). Compound **14d**: **2-Methylthio-6-diphenylmethylidene-4-*m*-tolyl-1,3-thiazine-5-carbonitrile** was also isolated as by-product. Yield 28% (0.059 g). Mp 188.5-189.5 °C (EtOAc-hexane). δ_H ($CDCl_3$) ca. 7.65-7.61 (m, 2H, Ar), 7.41-6.99 (m, 12H, Ar), 2.57 (s, 3H, CH_3), and 2.38 ppm (s, 3H, SCH_3). δ_C ($CDCl_3$) 166.7, 158.5, 146.6, 139.6, 137.9, 136.1, 131.2, 130.7, 130.4, 129.4, 129.1, 128.6, 128.2, 126.2, 21.5, and 15.0 ppm. ν_{max} (KBr) 3040, 2910, 2209 (CN), 1499, 1443, 1312, 1192, 1157, 1115, 1076, 1030, 972, 927, 885, 835, 795, 768, 700, 681, 637, 613, 584, 519, and 442 cm^{-1}. UV-Vis λ_{max} (EtOH) 250.0 (log ε 4.78), 297.5 (4.84), and 408.5 nm (4.21). (Found: C, 73.56; H, 4.89; N, 6.35; S, 1488. $C_{26}H_{20}N_2S_2$ requires C, 73.55; H, 4.75; N, 6.60; S, 15.10%)

Thermal Rearrengiment of 3'-Methyl-2-methylthio-5-methylsulfonyl-4,3'-diphenyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane (12e) to Methyl 5-Methyl-3-methylsulfonyl-2,5-diphenyl-4-thioxopyrroline-1-dithiocarboxylate (13e). 3'-Methyl-2-methylthio-5-methylsulfonyl-4,3'-diphenyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane (**12e**) (0.217 g, 0.5 mmol) was refluxed for 10 min in benzene (50 mL) and evaporated to dryness. The residue was column chromatographed (silica gel 60, 400 mesh, benzene), and recrystallized from benzene-hexane. Yield 100% (0.217 g). Red prisms. Mp 217.5-226.0 °C. δ_H ($CDCl_3$) ca. 7.5 (m, 10H, 2 × C_6H_5), 3.24 (s, 3H, SO_2CH_3), 2.31 (s, 3H, SCH_3), and 2.04ppm (s, 3H, CH_3). δ_C ($CDCl_3$) 222.9, 204.4, 173.3, 138.7, 131.6, 130.6, 129.0, 128.3, 127.7, 125.7, 88.6, 42.7, 25.3, and 21.7 ppm. ν_{max} (KBr) 2922, 1510, 1468, 1445, 1370, and 1142 (SO_2), 1312, 1275, 1219, 1165, 1040, 961, 910, 862, 791, 764, 743, 721, 696, 658, and 629 cm^{-1}. UV-Vis λ_{max} (EtOH) 210.5 (log ε 4.38), 264.5 (3.66), 297.0 (3.85), 333.0 (3.73), 402.5 (4.14), and 471.0 nm (3.01). (Found: C, 55.61; H, 4.55; N, 3.12; S, 29.88. $C_{20}H_{19}NO_2S_4$ requires C, 55.40; H, 4.42; N, 3.23; S, 29.58%)

X-Ray crystallographic data of compound **13e**;

Empirical Formula	$C_{20}H_{19}O_2NS_4$
Formula Weight	433.62
Crystal Color, Habit	red, prism
Crystal Dimensions	0.30 × 0.25 × 0.25 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 17.783(1) Å
	b = 23.259(2) Å
	c = 10.0808(8)Å
	V = 4169.5(5) $Å^3$

Space Group	Pbca(#61)
Z value	8
μ (MoKα)	4.71 cm^{-1}
No. of Reflections Measured	Total: 9579
	Unique: 4748 (R_{int}= 0.053)
No. Observations (I>1.50σ(I))	2723
Residuals: R; Rw	0.036; 0.043

Reverse Rearrangement of Ethyl 1-Methylthiothiocarbonyl-4-thioxo-2,5,5-triphenylpyrroline-3-carboxylate (13c) into Ethyl 2-Methylthio-4,3',3'-triphenyl-1,3(6*H*)-thiazine-6-spiro-2'-thiirane-5-carboxylate (12c). The solution of ethyl 1-methylthiothiocarbonyl-4-thioxo-2,5,5-triphenylpyrroline-3-carboxylate (**13c**) was refluxed in xylene at 140 °C for 1 h. The solvent was evaporated to dryness in vacuo and the residue was column chromatographed (silica gel 60, 400 mesh, EtOAc : pentane = 1 : 10). Reversely rearranged ethyl 2-methylthio-4,3',3'-triphenyl-1,3-thiazine-6-spiro-2'-thiirane-5-carboxylate (**12c**) was obtained in 35% yield and 42% of compound **13c** was recovered. On the other hand, when the above solution was continued to reflux for 1 day, compound **12c** could not be obtained, but desulfurized ethyl 6-diphenylmethylidene-2-methylthio-4-phenyl-1,3-thiazine-5-carboxylate (**14c**) was formed in 48% yield and compound **13c** was recovered in 14% yield.

Thermal Decomposition of Methyl 3-Cyano-5,5-diphenyl-4-thioxo-2-*m*-tolylpyrroline-1-dithiocarboxylate (13d). Looking forward to similar reverse rearrangement to take place for compound **12d**, the solution of methyl 3-cyano-5,5-diphenyl-4-thioxo-2-*m*-tolylpyrroline-1-dithiocarboxylate (**13d**) was also refluxed in xylene at 140 °C for 1 h, but compound **12d** was never obtained. (Compound **13d** was recovered in 76% yield.) Moreover, prolonged heating of the above solution in xylene for 24 h at 140 °C merely gave 2-methylthio-6-diphenylmethylidene-4-*m*-tolyl-1,3-thiazine-5-carbonitrile (**14d**) in 71% yield.

REFERENCES AND NOTES

1. Paper 7 in this series; T. Yamamoto and M. Muraoka, *J. Heterocycl. Chem.*, 1988, **25**, 835.
2. T. Yamamoto, M. Itoh, N. U. Saitoh, M. Muraoka, and T. Takeshima, *J. Chem.Soc., Perkin Trans. 1*, 1990, 2459.
3. T. Yamamoto, M. T. Imagawa, Y. T. Yabe, E. M. Suwabe, and M. Muraoka, *J. Chem.Soc., Perkin Trans. 1*, 1990, 3003.
4. I. Shahak, Y. Sasson, and Y. Wolman, *Synthesis*, 1974, 281.
5. E. Schaumann, E. Kausch, S. Grabley, and H. Behr, *Chem. Ber.*, 1978, **111**, 1486.

6. V. A. Renznikov and L. B. Volodarskii, *Izves. Akad. Nauk SSSR, Ser. Khim.*, 1990, 390.
7. M. Muraoka, T. Yamamoto, and T. Takeshima, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 2462.
8. M. Muraoka, T. Yamamoto, S. Yamaguchi, F. Tonosaki, T. takeshima, and N. Fukada, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1273.
9. M. Muraoka, T. Yamamoto, T. Ebisawa, W. Kobayashi, and T. Takeshima, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1017.
10. T. Yamamoto, M. Muraoka, and T. Takeshima, *J. Chem. Res. (S)*, 1979, 384.
11. T. Yamamoto, M. Muraoka, M. Takahashi, and T. Takeshima, *J. Chem. Res. (S)*, 1980, 148; *J. Chem. Res. (M)*, 1980, 2059.
12. T. Yamamoto and M. Muraoka, *J. Chem. Res. (S)*, 1982, 274; *J. Chem. Res. (M)*, 1982, 2816.
13. M. Muraoka and T. Yamamoto, *J. Heterocycl. Chem.*, 1984, **21**, 1445.
14. T. Yamamoto and M. Muraoka, *J. Chem. Res. (S)*, 1984, 266.
15. M. Muraoka, A. Yamada, and T. Yamamoto, *J. Heterocycl. Chem.*, 1984, **21**, 953.
16. T. Yamamoto and M. Muraoka, *J. Heterocycl. Chem.*, 1988, **25**, 835.
17. J. Miller, *J. Org. Chem.*, 1956, **24**, 560.
18. C. G. Overberger and J.-P. Anselme, *J. Org. Chem.*, 1963, **28**, 592.
19. E. K. Marshall and S. F. Acree, *Ber.*, 1910, **43**, 2323.